Dielectrics Newsletter
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The Dielectric Properties of Ion - Conducting Polymers

The complex dielectric function $\varepsilon^*(\omega)$ and hence the complex conductivity $\sigma^*(\omega) = i\cdot\varepsilon_0\cdot\omega\cdot\varepsilon^*(\omega)$ (with ε_0 being the permittivity of free space) is a key feature of ion conducting polymers. It allows analysing the underlying mechanisms of charge transport if measured over a wide enough frequency and temperature range (DC to 10^9 Hz, 100 K – 400 K). Thereby the frequency and temperature dependence of the conductivity reflects a continuous process: At low frequency the outer electrical field forces the charge carriers to drift over large distances r compared to a separation ξ between neighbouring sites; with increasing frequency the mean displacement r of the charge carries is reduced. When the condition $r \ll \xi$ is fulfilled the conductivity follows the power law $\sigma^*(\omega) \sim \omega^s$ with $0 \leq s \leq 1$ being characteristic for hopping conduction. Thus the frequency dependence of the conductivity at a certain temperature reflects the effective topology of the conducting pathes at this temperature [1-3].

In this paper the above mentioned frequency and temperature dependence will be exemplified for a typical ion conducting polymer, a so called "Ionene" [4-8]. The resulting frequency and temperature dependence will be discussed qualitatively in the framework of the existing theoretical approaches, which are in part based on the Debye-Hückel-Falkenhagen theory.

"Ionenes" are polyelectrolytes with quarternized N-cations as part of their repeat units, for which poly(dialkyliminoalkylene) salts are typical examples

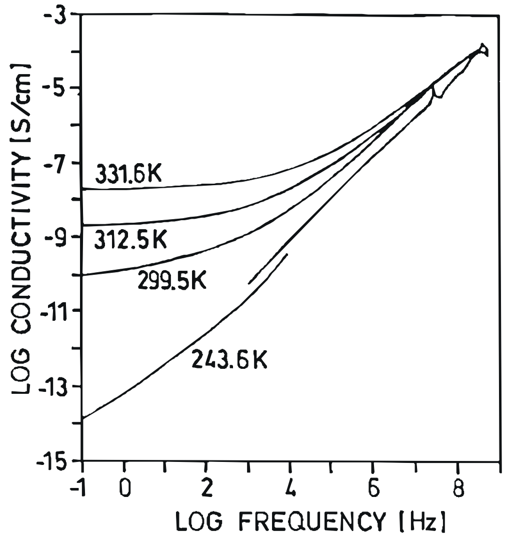
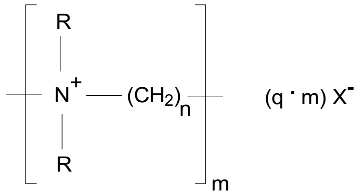


Fig.1 Frequency and temperature dependence of the real part of the complex conductivity σ^*. Sample Ionene with m = 6, n = 10, R = CH3, X = BF4.



$$\left[\begin{matrix} R \\ | \\ -N^{+}-(CH_2)_n- \\ | \\ R \end{matrix}\right]_m \quad (q\cdot m)\,X^-$$

m,n = 6,10,20, X = monovalent (q =1) or bivalent (q = 0.5) counterion, R = CH2 CH3, CH3. Ionenes form amorphous glassy films when quenched from the melt or cast from solution followed by rapid evaporation of the solvent [6]. The glass transition temperature Tg determined by DSC is found to be between 255 K and 470 K depending on the structure of the polymer and the type of counterion X.

The dielectric properties of the ionenes were studied in the frequency range between 10^{-1} Hz and 10^9 Hz and at temperatures between 100 K and 350 K. The glassy polymers exhibit a dielectric relaxation at low temperatures which is assigned to a coupling of the motion of the methylene groups to the ionic centres in the polymer chain [4-6]. At the higher temperature (T > 250 K) the dielectric properties are dominated by a conductivity contribution characterized by an increase of the dielectric loss with decreasing frequency and increasing temperature. For the real part σ' of the complex conductivity σ^* a frequency and temperature dependence as shown in Fig. 1 is observed.

The frequency and temperature dependence is characterized by the following features:

1. The real part of the conductivity increases with increasing frequency and temperature.
2. For high temperatures the conductivity is almost constant at low frequencies but increases at the critical frequency ν_{crit} where the change of the slope versus frequency is maximal.
3. This ν_{crit} shifts to lower values with decreasing temperature.
4. Above ν_{crit} the frequency dependence of the conductivity is

proportional to ω^s with $0 \leq s < 1$.
5. At low temperature the real part of the conductivity σ' is proportional to ω^s with $s \cong 1$.
6. The exponent s in the power law $\sigma' \sim \omega^s$ is a function of both frequency and temperature. Similar features have been observed in inorganic glasses as well [13].

The underlying mechanism of charge transport is still a controversial topic [9-21]. Several microscopic models describe the above mentioned qualitative features of the frequency and temperature dependence of the conductivity:
1. The diffusion-controlled relaxation model [14], which does not assume a distribution of relaxation times as often invoked to explain frequency-dependent relaxation data.
2. An effective medium theory of the motion of ions and/or defects in an amorphous matrix based on a hopping model with randomly distributed sites and activation energies [15,16].
3. The jump relaxation model [17,18] in which a dynamical cage surrounding an ion is introduced- in analogy to the Debye-Hückel-Falkenhagen theory [19,20]. The hopping motion of the mobile charged defects is strongly influenced by their mutual repulsive interaction and therefore, their jump diffusion is not a random process. Instead correlated forward-backward hopping sequences are the elementary step of jump relaxation.

One has to assume that several of the above mentioned mechanisms of charge transport are present in parallel in ion conducting polymers, like ionenes.

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Book Review : Liquid State Electronics of Insulating Liquids

by Werner F. Schmidt,
CRC Press LLC Boca Raton New York 1997, 350 pages, hardcover.
ISBN 0-8493-4445-X

With this book an attempt is made to present a concise description of the electronic properties of nonpolar dielectric liquids and some related materials. The topics discussed form part of a field which in analogy to solids or gases may be called liquid-state electronics. The main emphasis is on electronic processes, but ionic and other types of charge transport are included where appropriate. The book addresses itself to physicists and chemists in industrial, governmental and university laboratories, to electrical and electronic engineers, and to materials scientists. It is also intended to provide graduate students with the necessary fundamental knowledge on the experimental techniques and the theoretical concepts employed in research on insulating materials.

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Broadband Dielectric Measurement Techniques – Recent Progress

High resolution measurements in the frequency range from 10^{-4} Hz – 10^{7} Hz are based on frequency response analysis. Recently Novocontrol GmbH launched a new system "Alpha High Resolution Dielectric Analyzer". Its performance – especially in comparison to the combination Broadband Dielectric Converter BDC + frequency response analyzer (FRA) - is examined and presented in the following measurements.
As a low loss test sample, an air capacitor mounted in the sample cell of each system was used. It was prepared from parallel gold plated electrodes with 30 mm diameter. The electrode distance was adjusted to 50 µm by two silica spacer rods resulting in about 125 pF capacity.
Due to the conductance of the rods, the capacitor shows especially at ambient temperature remaining losses. By cooling the capacitor to low temperatures, the conductivity of the spacer rods decreases and the losses are continuously reduced. This kind of capacitor is well suited for testing the tan(δ) accuracy and resolution of dielectric analysis systems. Results for three different temperatures are shown in Fig. 1. At -50°C and

frequencies above 10 Hz, the capacitor losses are approx. tan(δ) ≈ 10^{-4}. At lower frequencies tan(δ) increases to about $3\cdot10^{-4}$ at 0.1 Hz. This dependency can be measured without significant noise by the Alpha analyzer at frequencies below 100 kHz. The combination BDC + FRA shows the same dependency, but superimposed by about 100% noise due to the system resolution limit tan(δ) of 10^{-4} which is in the same order as the sample loss.

If the temperature is lowered to -100°C and -140°C, the capacitor losses decrease further and the better resolution limit of the Alpha analyzer is the limiting factor as shown in the lower two diagrams of Fig. 1. Compared to the BDC + FRA combination, the resolution is improved from 10^{-4} to 10^{-5}. At the high frequency end above 100 kHz, the results show an increase in tan(δ) which is not intrinsic to the sample, but due to high frequency limitations for both systems. At 10 MHz, the accuracy is decreased to about tan(δ) ≈ 0.01 corresponding to about 1° phase accuracy.

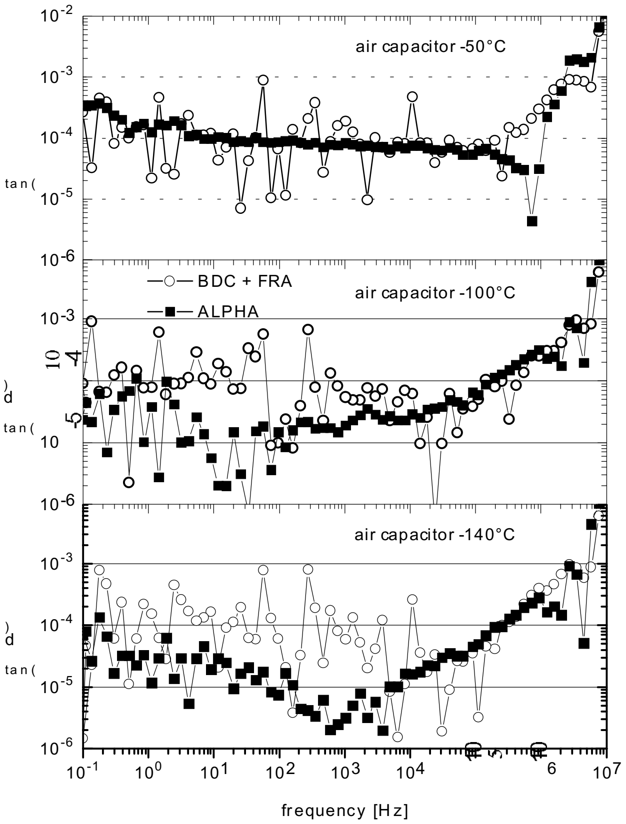

Fig. 1 : tan(δ) of an air capacitor (thickness: 50 µm, diameter: 30 mm) at different temperatures measured Alpha Dielectric Analyzer (solid squares) and the combination Broadband Dielectric Converter BDC + frequency response analyzer (open circles)

Fig. 2 shows similar measurements for a low loss Polyethylene sample at ambient temperature. The sample capacity is about 160 pF and in good agreement for both systems. The difference of about 1% in the absolute value is due to stray capacities and mounting deviations of the different sample cells. The tan(δ) of the sample is between 10^{-4} .. $3\cdot10^{-4}$. The results of the two measurement systems show the same behaviour as for the low loss capacitor. Whereas for the BDC + FRA combination the phase resolution limit is reached, the results can be resolved with only 10% scatter by the Alpha. The tan(δ) increase at high frequencies is again due to internal limitations of both systems. This limitation can be seen in the capacity too. The deviations at 10 MHz are about 1.5pF for the Alpha and about 8pF for the BDC + FRA combination.

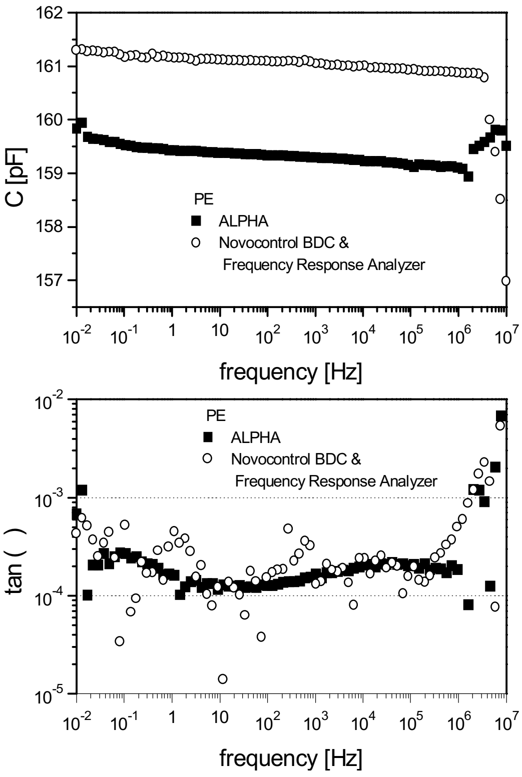

Fig. 2 : Capacitance C and tan(δ) of a Polyethylene (PE) sample (thickness: 40 µm, diameter: 20 mm) otherwise as Fig. 1.

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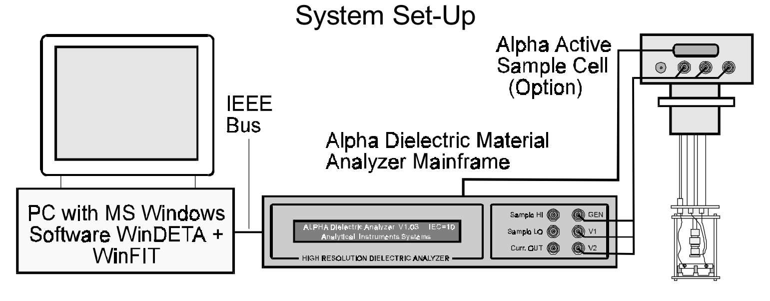
New Integrated Dielectric Analyzer Extends Accuracy and Impedance Range for Material Measurements

Novocontrol spectrometers for dielectric and impedance material analysis have a world-wide reputation for highest quality and flexibility. Several systems for dielectric- and impedance spectroscopy over a frequency range from µHz up to GHz are available. Sample cells are offered in standard parallel plate transmission and reflection geometry, four wire contact arrangement and as interdigit comb electrodes. This allows characterization of solid materials, liquids, powders and thin films. Several temperature control systems covering a range from -160°C .. 500°C are available. Due to a modular concept, each impedance analysis system can be combined with each temperature control system and most of the sample cells. Automatic system and experiment control and sophisticated data evaluation is performed by WinDETA and WinFIT software packages which have established a world-wide standard in dielectric material analysis.

In spite of this exceptional performance, users often are demanding for an even more sophisticated solution. Especially for low loss materials there is a strong interest in improved accuracy. Another improvement often suggested is to extend the impedance range to low impedance. Last but not least, there seems to be a requirement for an integrated single device measurement system optimized for material analysis and especially dielectric spectroscopy. With the Alpha high resolution dielectric material analyzer, Novocontrol presents such a system for the first time. The Alpha is offered from now on as standard solution for the frequency range below 10 MHz.



The sample current is converted by the Alpha-S active sample cell into two voltages which phases and amplitudes are measured by the Alpha analyzer. Device control, calibration, data evaluation, visualization and export are computer supported by WinDETA / WinFIT software.

New approach to material analysis

The Alpha measures complex impedance Z'+jZ" in the frequency range from 3 µHz .. 10 MHz. The instrument can be used as a general purpose precision impedance analyzer, but has been especially designed for dielectric and impedance material analysis. By combining a series of exceptional features in a single, compact case, the Alpha defines a new milestone in economical high performance instrumentation.

Characterization of low loss dielectrics

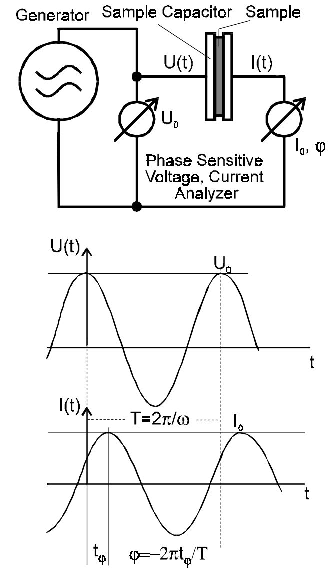
Due to the extraordinary high upper impedance limit of > 10^{14} Ω nearly all kind of dielectrics and isolators can be measured even down to very low frequencies below the mHz range. The high accuracy in loss factor $\tan(\delta) < 3\cdot10^{-5}$ (resolution < 10^{-5}) provides access to material properties not available until now. Even lowest loss materials used in ceramic capacitors, isolators in power industry or weakest molecular relaxations processes can now be analyzed over a wide frequency range.

No limitations : High and low conductive materials

In contrast to other dielectric analysis systems, the Alpha is not limited to high impedance dielectric samples. The lower impedance limit < 0.1 Ω allows also to analyze conductive samples like semiconductors, electrolytes and electrochemical systems. As the complete impedance range of 15 orders of magnitude is accessible with one device, even samples with for instance temperature induced metal insulator transitions can be measured.

Specified at the sample position

In the Alpha-S version, the impedance converter is directly mounted on top of the sample cell connected by rigid lines. This set-up guarantees high accuracy up to 10 MHz and enables optional



$$U(t) = U_0 \cos(\omega t)$$

$$I(t) = I_0 \cos(\omega t + \varphi) =: re(I^* \exp(j\omega t))$$

Fourier Transform over n Periods

$$I^*(\omega) = I' + iI'' = \frac{2}{nT}\int_0^{nT} I(t) \exp(i\omega t)\, dt$$

$$I_0 = \sqrt{I'^2 + I''^2}; \quad \tan(\varphi) = \frac{I''}{I'}$$

$$\text{Impedance } Z^*(\omega) = Z' + iZ'' = \frac{U_0}{I^*(\omega)}$$

Permittivity

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' = \frac{-i}{\omega Z^*(\omega)} \frac{1}{C_0}$$

C_0 Empty Cell Capacity

Conductivity

$$\sigma^*(\omega) = \sigma' - i\sigma'' = \frac{1}{Z^*(\omega)} \frac{d}{A}$$

d Electrode Spacing; A Electrode Area

Fig. 2 : Principles of impedance and material measurement.

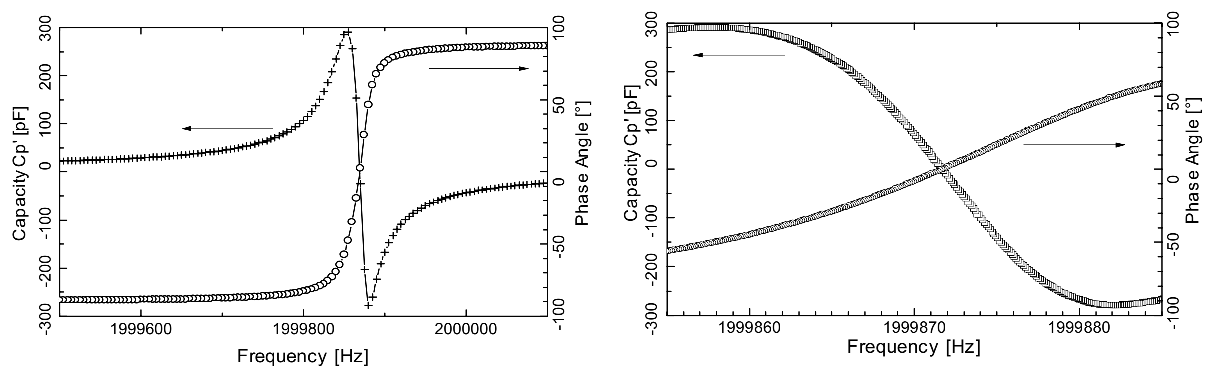


Fig. 4 : Dielectric properties of a 2 MHz quartz crystal, half power bandwidth ≅ 30 Hz, 0.1 Hz frequency resolution

control of sample temperature. The accuracy specification for material measurements applies to the sample position, offering a turnkey solution without calibration errors due to cable inductance, contacts, stray capacities, grounding and shielding.

Innovative technology

The Alpha was completely new developed in 1998 based on state of the art digital signal processing techniques. Automatic device control including self calibration is provided by Novocontrol MS-Windows software WinDETA.
As shown in fig. 2, the basic operation is to create a sine wave at the frequency of interest, apply it to the sample and measure the sample voltage U(t) and result current I(t). From this, the amplitude I_0 and phase angle φ of the current harmonic base wave component $I^*(\omega)$ is calculated by complex Fourier transform (FT) of I(t). In addition to the phase detection, the FT suppresses all frequency components in I(t) except a narrow band centered around the generator frequency. This improves accuracy and reduces noise and DC drifts by several orders of magnitude. E.g. measuring a signal covered by a noise signal of 1000 times larger is possible. Finally, the impedance $Z(\omega)$ and material parameters $\varepsilon^*(\omega)$ and $\sigma^*(\omega)$ are calculated.

Digital signal synthesis

Such kind of set-up is implemented in the Alpha as shown in fig. 3. A digital signal processing system is used both for frequency generation and analysis of the input signals. The generator signal is directly digitally synthesized over the entire frequency range. The signal processor continuously calculates with 50 MHz rate digital sine wave values which are transformed into a sine wave voltage. This is done by a high speed digital to analogue (DA) converter followed by a higher harmonic filter. This kind of signal generation guarantees highest stability and a frequency resolution of 32 bit corresponding to e.g. 10 mHz out of 20 MHz (optional 40 MHz).

Digital signal analysis

The voltages from two independent input channels are amplified, filtered and converted into two digital data streams which are phase sensitive digitally on-line analyzed with respect to their harmonic base waves by discrete Fourier transform (DFT).
Channel 1 measures directly the voltage V1 applied to the sample. The resulting sample current Is is transformed by a wide current - wide frequency range precision impedance converter into the voltage V2 measured by channel 2.

Reference technique

Most of the signal generation and analysis is performed in the digital system part. Therefore phase and stability errors in this part can be minimized to neglectible values. In

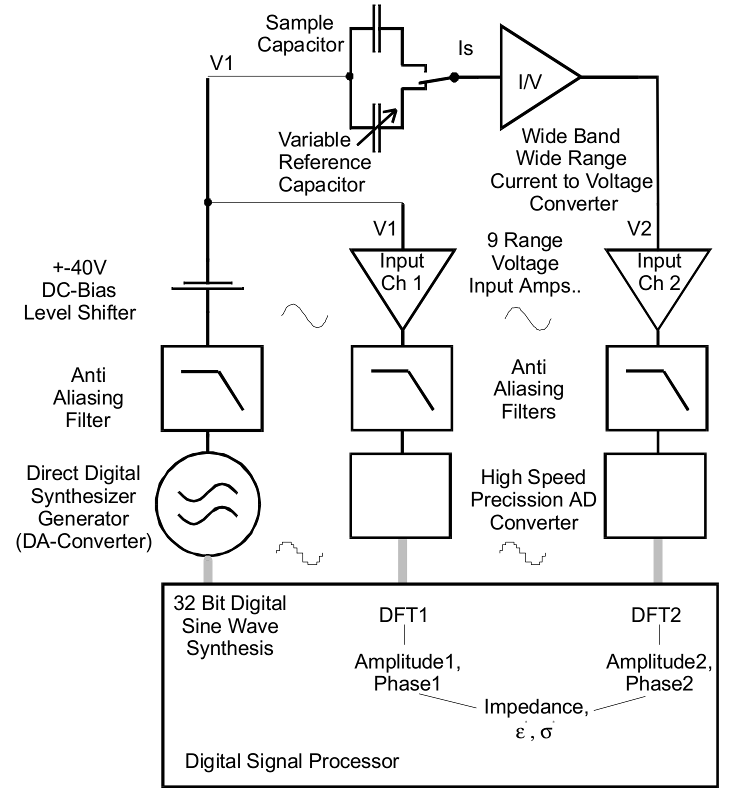


Fig. 3 : Basic Alpha analyzer set-up. For details, see text.

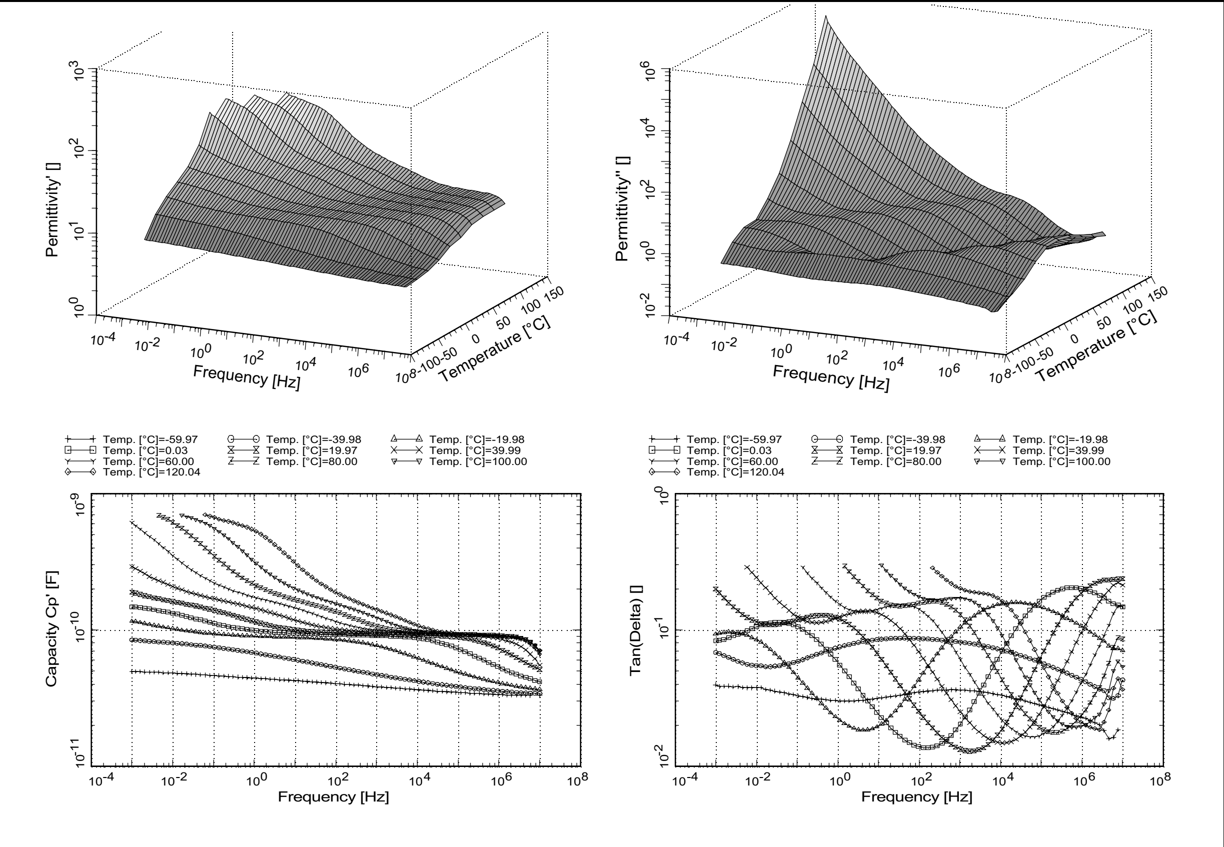


Fig. 5 : PVDF results : 3D representation of permittivity, 2D diagrams for measured capacity and loss factor tan(δ)

order to reach similar high accuracy in the analogue systems components too, the Alpha uses a special reference technique known of the Novocontrol Dielectric Converter BDC. After each direct measured impedance point, the sample is replaced by a precision low loss reference capacitor. The reference measurement includes all linear systematical deviations of the system and therefore can be used in order to eliminate them. This technology in combination with straightforward digital design enables the high accuracy required for material analysis and especially spectroscopy of low loss dielectrics.

Measurement examples

The performance for low loss materials is shown and discussed in a preceding article of this newsletter. The measurements in Fig. 4 and 5 were done with a Alpha analyzer with active sample cell and a Quatro Cryosystem system for temperature control. In order to demonstrate the overall system performance PVDF /1/ was chosen as a material with not too low losses. Fig. 5 shows the dielectric spectrum for frequencies from 1 mHz .. 10 MHz at several temperatures. PVDF shows an α and β relaxation with tan(δ) losses in the range 0.01 .. 0.2. At higher temperatures, DC conductivity creates low frequency increase of ε''. As shown in the 3 dimensional diagrams, the data could be measured over the entire frequency and temperature range nearly without artefacts. In order to show the data more detailed, the diagrams for capacity and tan(δ) were confined to the range of interest.

For demonstration of the Alpha frequency resolution and stability, a commercial high Q quartz crystal used as frequency standards e.g. in clocks and similar kind of electronic devices was measured. The crystal was mounted in the Alpha active sample cell and temperature stabilized to 20°C +- 0.01°C. Fig. 4 shows the dielectric properties with the typical resonant behaviour with 5 Hz (left diagram) and 0.1 Hz (right diagram) resolution. The resonance frequency f_0 is at 1999871.8 Hz with a half power width of ≅ 30 Hz. Below f_0, the device behaves like a 22 pF capacitor with -90° phase shift. With increasing frequency the real part of capacity Cp' and the phase shift increases, too. At f_0 the impedance becomes purely resistive indicated by vanishing Cp' and phase shift. Above f_0, the impedance changes to inductive behaviour corresponding to 90° phase shift and a corresponding negative Cp'. As shown in fig. 4, even at 0.1 Hz resolution, the measurements are free from significant artefacts and noise. It should be emphasized, that each data point is independently measured without averaging or correlation to neighboured points and that there is no synchronization between the sample crystal and the Alpha internal oscillator.

/1/ PVDF samples were supplied by Elf Atochem France, Materials Research Lab., Dr. B. Ernst, F-27470 Serquigny

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OVERVIEW
BROADBAND DIELECTRIC SPECTROSCOPY
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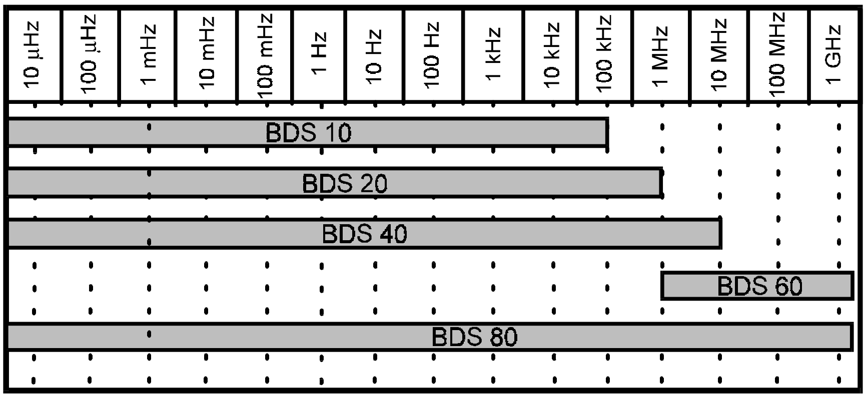

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Dielectric Spectrometers and Modules

☐ Economical dielectric spectrometers (3 µHz - 100 kHz or 3 µHz - 1 MHz)

☐ Broadband dielectric spectrometer (3 µHz - 10 MHz)

☐ RF dielectric spectrometer (1 MHz - 1.8 GHz)

☐ Temperature control systems (+20°C .. +400°C or -100°C .. +250°C or -160°C to +500°C)

☐ Broadband Dielectric Converter

☐ MS-Windows software for automatic measurement of dielectric relaxations, impedance, electrical and magnetic material properties

☐ MS-Windows software for automatic curve fitting data analysis (WLF, VF) and equivalent circuit transformation

New Instruments

☐ TSDC Instruments and WinTSC software

☐ Pressure dependent dielectric spectrometers

☐ ALPHA high resolution dielectric analyzer

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